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Laboratory test of source encapsulation for decreasing PCB concentrations.

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SUMMARY
This study investigates the effect of encapsulation of tertiary PCB sources with PERMASORB™ Adsorber Wallpaper and the surface emissions trap (cTrap) on indoor air concentration of PCBs and on the PCB content in the source. The 40 weeks long laboratory investigation shows reduction of the air concentration by approx. 90% for both wallpapers, a level comparable to source removal. The potential for extraction of PCBs from the contaminated materials stays unclear for both wallpapers. The cTrap has shown potential to accumulate PCBs, however the total content of PCB in investigated sources has apparently increased. The opposite was observed for the PERMASORB™, where the total PCB content in the sources has decreased, with however only small concentration of PCBs in the wallpaper measured at the end of the experiment.

PRACTICAL IMPLICATIONS
The removal of primary sources of PCB has often been insufficient for lowering the high indoor air levels, and removal of secondary and tertiary sources is often complicated and costly. Encapsulation of PCB sources could be considered in order to decrease the costs of remediation, or as a temporary solution, when immediate source removal is not possible.

KEYWORDS
Polychlorinated biphenyls, remediation, cTrap, PERMASORB™ Adsorber Wallpaper

1 INTRODUCTION
Polychlorinated biphenyls have been broadly used since the fifties and during the following three decades. Primary sources, which are products originally containing PCBs, include electrical transformers and capacitors as well as soft and flexible construction products e.g. sealants. The manufacture and use of PCB containing construction products was banned in the late seventies due to persistency and accumulation in food chains with negative impact on environment and human health. In 2013 PCBs were classified as carcinogenic to humans with class 1 (Lauby-Secretan et al. 2013).

In Denmark, the Danish Health Authority introduced recommended action limits for PCBs in indoor air. The limits are based on PCB_{total}, calculated as sum of 6 congeners (PCB-28, 52, 101, 138, 153 and 180) multiplied by factor 5. Shortly, exposure to levels between 300 and 3000 ng/m^3 is considered to pose a possible health risk and an action plan would be needed to bring levels down. Immediate action is required if the indoor air levels exceed 3000 ng/m^3 (The Danish Health Authority, 2013).

Over the last 40-70 years, PCB has migrated from their primary sources contaminating other surfaces either by diffusion to adjacent materials (secondary sources) or by adsorption from contaminated air (tertiary sources) (Kolarik et al. 2014). The removal of primary sources only, has often been insufficient for acceptable lowering of high indoor air concentrations. Recently our group has shown that the impact of the tertiary sources on the indoor air concentrations can be substantial (Kolarik et al. 2014). Reduction of the impact from secondary and tertiary sources is therefore needed for the proper remediation of the contaminated buildings, but it significantly increases the costs. Encapsulation of PCB sources could be considered in order to decrease the costs of remediation, or as a temporary solution, when immediate source removal is not possible.

This study investigates applicability of two wallpapers, PERMASORB™ Adsorber Wallpaper and the surface emissions trap (cTrap) for PCB encapsulation. Application of PERMASORB™ for PCB encapsulation was tested before by the manufacturer showing reduction in the PCB air concentrations by 90% (Competenza GmbH rapport, 2013). The cTrap has never before been tested for PCB but was proven to reduce emission of selected VOCs by 98% and block particle-bound emissions such as mycotoxins (Markowicz and Larsson, 2013; 2015). The aim of this study was to investigate the effect of encapsulation of the tertiary PCB sources by means of those two wallpapers and to compare the effect on indoor air concentrations with source removal. It was also the aim to investigate the ability of wallpapers to reduce PCB contamination in source's upper layers.

2 MATERIALS/METHODS

Experimental design

The experiment was conducted at Danish Building Research Institute, in small scale, 51 L, climate chambers (CLIMPAQ). The sources of PCB used in the present investigation are blocks of concrete originating from inner walls of PCB contaminated apartments. At the renovation site, the blocks were cut from inner walls far from primary sources (at least 30 cm), thus could be considered as tertiary PCB sources, contaminated by absorption from indoor air (Liu et al. 2015). The housing estate is described elsewhere (Frederiksen et al. 2012; Kolarik et al. 2014). The average temperature during the whole experiment was 22.7±2.1^{o}C. The air concentrations presented in this paper were adjusted to 23°C according to the method described in Lyng et al. (2015). To adjust for variations in air change rate within the time of experiment and between the climate chambers, the results of air analyses are shown as emission rates.

The handling of concrete blocks is shown in Table 1. Eight weeks prior to encapsulation, approx. 6.5 x 6 x 45 cm blocks of concrete (with original paint) were placed in 6 climate chambers and 2 chambers were left empty. At time 0, the sources were removed from the climate chambers. Two sources were wrapped in PERMASORB™ wallpaper and 2 were wrapped in cTrap and immediately placed back into their original chambers. The chambers were opened and closed as quickly as possible in order to limit unintended emission. Two sources were permanently removed. In addition, one source encapsulated with PERMASORB™ and one with cTrap was placed in each of the two empty chambers in order to better investigate tightness of the encapsulants.

Table 1. Handling of concrete blocks

Chamber	Time, weeks	
	-8	0 - 40
1	Unwrapped source	Source removed/Empty
2	Unwrapped source	Source removed/Empty
3	Unwrapped source	Source wrapped in PERMASORB™
4	Unwrapped source	Source wrapped in PERMASORB™

5	Empty	Source wrapped in PERMASORB™
6	Unwrapped source	Source wrapped in cTrap
7	Unwrapped source	Source wrapped in cTrap
8	Empty	Source wrapped in cTrap

Measurements and chemical analysis

The air samples were taken 3 days before encapsulation (shown as -3 days in the result section) and then with one month interval during the following 40 weeks after encapsulation. The air was sampled for approx. 24 hours using pumps (GilAir 5, Sensidyne, US) connected to XAD-2/PUF sorbent tubes with quartz filter (SKC type 226-30-16, SKC Inc., Eighty Four, PA, USA), with a sampling flow of 1.9 L/min. All samples were frozen at -20°C immediately after the measurement and kept frozen until analysis. The analyses were conducted at accredited commercial laboratory (Dansk Miljøanalyse, Vedbæk, Denmark). The samples were extracted with mixture of cyclohexane and acetone in the ratio of 50/50 in an ultrasonic bath and analysed with GC-MS with added 13C-PCB-202 recovery standard and syringe standard of dibromooctaflourobiphenyl. Both sections in sorbent tubes were analysed together. The analyses included seven congeners: PCB-28, 52, 101, 118, 138, 153 and 180. The detection limit for each congener was 1 ng/m^3 and the expanded uncertainty was 20% per congener.

The sources were analysed twice: before they were placed in the climate chamber and after the 40 weeks of encapsulation exposure. The wallpapers were only analysed once, at the end of the experiment, as it was assumed that they initially were PCB-free. The layers were separated by first scraping the paint off and then scraping off the plaster. Using a water-cooled concrete cutter, the concrete was cut into the fractions shown in Figure 1 and crushed in a ball mill. The extraction and analyses were as described for the air samples. The limit of detection was 0.01 mg/kg for the individual congeners, and the uncertainty was 35%, however higher for the very low concentrations.

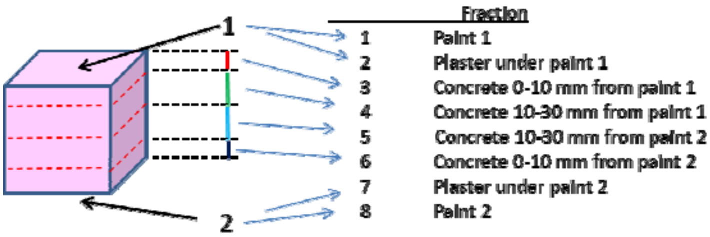

Figure 1. Analysed fractions of painted concrete blocks (PCB sources).

3 RESULTS

Time course of PCB concentration in the air

PCB-28 was measured in concentrations above detection limit in all samples and PCB-52 was detected in all but two samples. The concentrations of these two congeners were at similar level. PCB-101 was detected in most of samples taken before encapsulation, but dropped to levels close to detection limit or below it in the first weeks after encapsulation. The heavier congeners were only detected rarely.

Figure 2 shows the calculated emission rate of PCB-28 and PCB-52 over time of the experiment based on data normalised to 23°C. The two thicker lines (blue and red) show emission rate in the course of time when pollution sources were removed from the chambers.

It can be observed, that emission rate in the chambers, where PCB contaminated blocks of concrete were encapsulated with either cTrap or PERMASORB™ wallpapers, nicely follow this decrease, despite somehow higher initial emission level. It can also be observed, that the concentration in the two chambers, where already encapsulated sources were placed, is stable (green and orange lines). Figure 3 shows more detailed picture of concentration over time in these two chambers. There was some initial contamination in the chambers on the level of 40-60 ng/m^3 PCB_{total}. This initial concentration was never exceeded throughout the 40 weeks long experiment, which suggests both wallpapers to be effective encapsulants of PCBs.

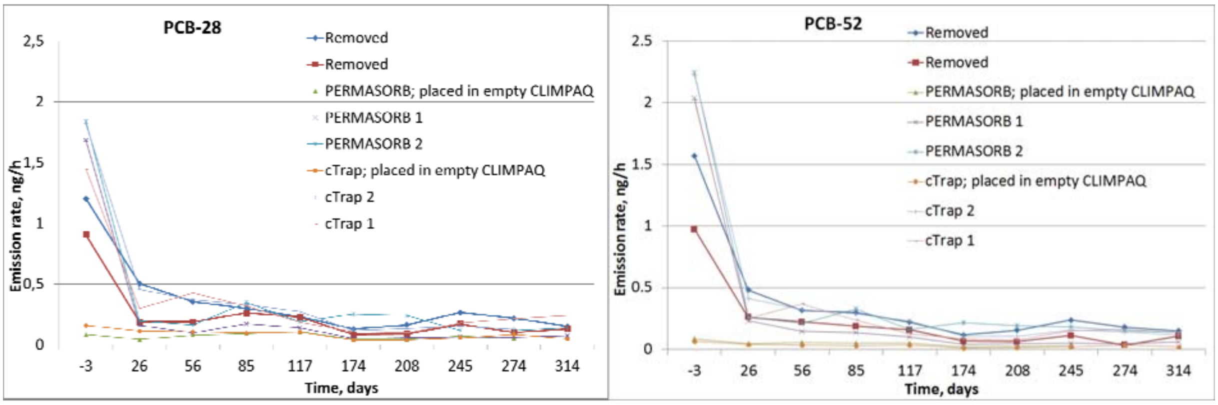

Figure 2. Emission rate of PCB-28 and PCB-52 measured in the chamber air with the source removed (2 replicates), sources encapsulated with PERMASORB™ and cTrap wallpapers (2 replicates of each). Orange and green lines correspond to sources encapsulated with cTrap and PERMASORB™ wallpaper placed in an empty chamber.

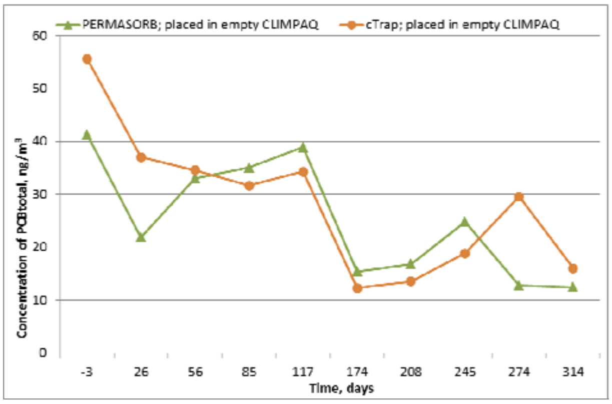

Figure 3. Concentration of PCB_{total} in two chambers, where encapsulated sources were placed into an empty chamber.

The effectiveness of the encapsulation is presented in Figure 4, which shows percentage reduction of the concentration in the chamber air with unwrapped sources (before encapsulation) air as function of time. Results for source removal are shown for comparison (blue and red trendlines). It must be underlined that in order to encapsulate or remove the sources, chambers needed to be open for a while, which has certainly impacted the already very high removal measured after 1 month. Slower process would therefore be expected in a real building. Nevertheless, the results suggests that both cTrap and PERMASORB™ are more effective than source removal in the first month, while after several months encapsulation with both wallpapers as well as source removal decrease the air concentration by approx. 90%, to the level comparable with background pollution of the chambers measured in this study.

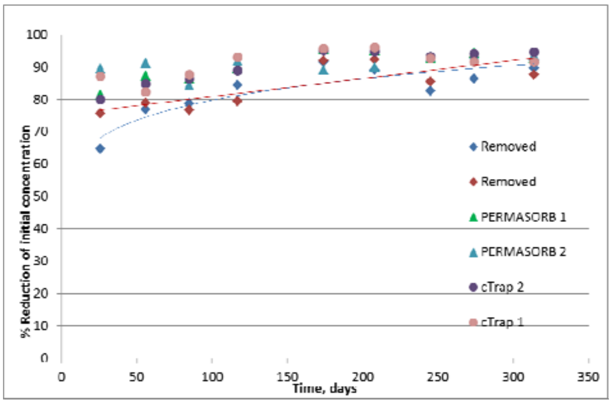

Figure 4. Reduction of PCB_{total} concentration in the chamber air. The blue and red line shows profiles for reduction of PCB_{total} concentration in the chamber's air after source removal

Concentration profiles in the sources (blocks of painted concrete)

Figure 5 shows difference between initial content of $\sum_7$PCB (sum of seven PCB congeners) in each faction of PCB source and $\sum_7$PCB content after the 40 weeks of encapsulation shown as percentage of the PCB content in the whole sample after the experiment.

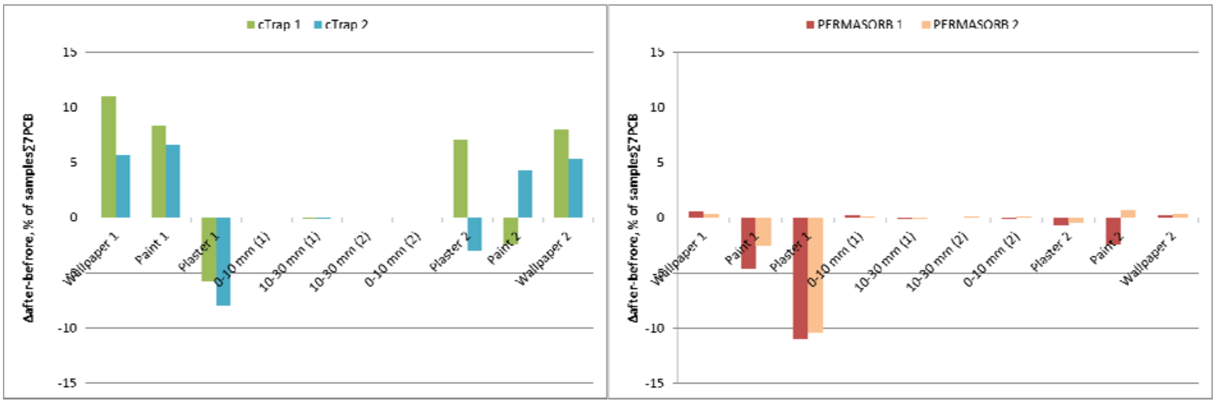

Figure 5. Difference between initial content of $\sum_7$PCB and content after 40 weeks among the fractions in relation to content in the whole sample after 40 weeks. Wallpaper 1 corresponds to either cTrap or PERMASORB™ attached to paint 1; further fractions follow Figure 1.

Some differences can be observed between the two types of wallpapers. The absorption of PCB to cTrap seems to be higher than to PERMASORB™. At the end of the experiment, PERMASORB™ contained approx. 0.4 % of the sample content of $\sum_7$PCB, corresponding to 1-2.5 ppm (depending on side and sample), while cTrap contained 5-11% of the sample content of $\sum_7$PCB, corresponding to 23-58 ppm. Furthermore the pattern of changes in the sample seems to be different for the two tested wallpapers. This difference is especially visible on one side of the sample (paint 1, Figure 5). While a few percent decrease in paint concentration was observed for PERMASORB™-encapsulated samples, increase of PCB concentration was seen in paint fraction of the samples encapsulated with cTrap. It should be further notified, that the total content of $\sum_7$PCB in the whole sample (sum of all fractions) has increased after the 40 weeks of experiment as compared to before levels when cTrap was used (1-35% increase), while it decreased in those samples where PERMASORB™ was used (5-15% decrease). This phenomenon is difficult to explain. There is quite a large uncertainty for the PCB measurement in concrete (35% per congener), the material samples are not completely homogeneous and there is some uncertainty related to separation of paint and plaster fractions (scraping) which could partly explain some of the results. However, since the replicates show the same tendency, this does not seem to be the only reason. The possible

absorption of PCB on both sides of cTrap (to one side from the sample and to the other side from the air) could explain both the higher concentration in the wallpaper and the total increase of PCB content in the sample. Figure 6 shows congener profiles in all fractions of one of the cTrap-encapsulated samples at the end of the 40 weeks period. Congener profiles of unwrapped source are shown for comparison. It can be seen, that PCB-28 has a higher relative abundance in the wallpaper (especially covering paint 1) compared to the other fractions of the sample, while PCB-101 and the other heavier congeners have lower relative abundance in the wallpaper compared to other fractions. PCB-28 is the most volatile of the measured PCBs and it is therefore one of the most frequently measured in the air. This air-like congener profile in the wallpaper confirms partly the hypothesis of absorption from the air.
As for the PERMASORB™-encapsulated samples, it would be expected, that decrease of PCB content in both plaster and paint as well as decrease of the total content of $\sum_7$PCB in samples resulted either in accumulation in the wallpaper or emission through the wallpaper to the air. None of those however have been observed. As shown in Figure 5, only small amounts of PCBs could be measured in PERMASORB™ wallpaper. It is therefore expected that extraction method applied by the laboratory was insufficient to extract PCB from this active charcoal-containing wallpaper. This issue needs to be further investigated.

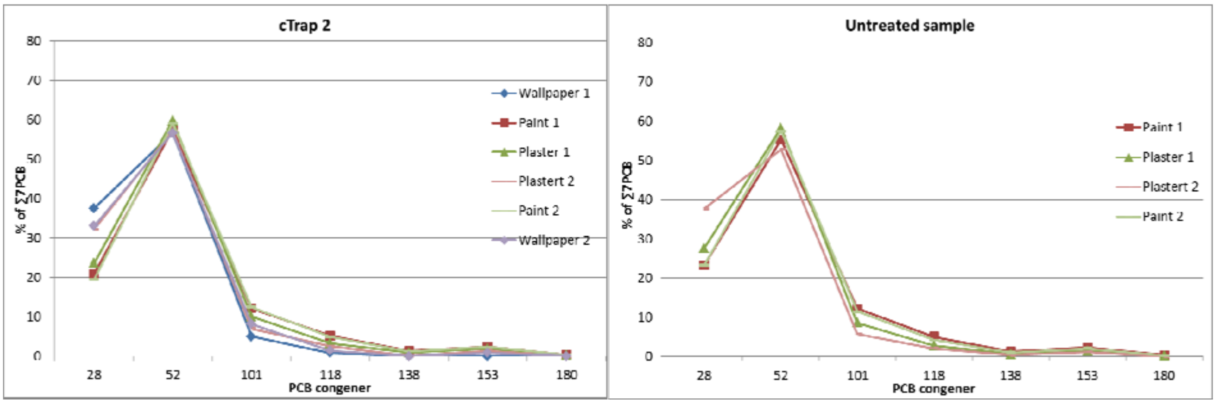

Figure 6. Congener profiles in different fractions of two cTrap encapsulated sources and two PERMASORB™-encapsulated sources shown as % of sum of 7 PCB congeners for each fraction. Results for a single block of concrete measured before the experiment are shown for comparison.

4 DISCUSSION

This study investigates encapsulation of tertiary sources of PCB with two types of wallpapers: the surface emission trap (cTrap) and the PERMASORB™ Adsorber Wallpaper in laboratory settings. The results show significant reduction of PCB-air concentrations after encapsulation, to the level that is comparable with source removal. Our investigation however does not explicitly support the ability of the wallpapers to accumulate PCBs and decrease its content in contaminated surfaces in the studied time span limited to 40 weeks.

The cTrap, is an adsorption cloth developed for reducing emission rates of volatile organic compounds and particulate matter from surfaces while allowing evaporation of moisture. It has previously been shown to efficiently reduce a range of VOCs including alcohols, aldehydes, ketones, terpenes, aromatic hydrocarbons, sulfides etc., in both laboratory and field investigation, as well as to block particle-bound emissions such as mycotoxins (Markowicz and Larsson, 2012 and 2015). The device has never been tested for SVOCs. The results presented in our study suggest cTrap to efficiently reduce PCB emission from contaminated concrete surfaces; however a field study is recommended to confirm the findings. Our investigation further shows that cTrap can accumulate PCBs, but it is unclear whether the accumulation has occurred on the air-exposed surface only, as no clear decrease in the total PCB content in the sample was measured.

The PERMASORB™ Adsorber Wallpaper has been developed for clean-up of tertiary sources of PCB in wall and ceiling paints and it has previously been tested by the producer. The chamber investigations of PERMASORB™ have shown 93% reduction compared to emission rate from the uncovered source. Field measurements conducted in 5 buildings over a 11 year period showed 92% - 98% reduction in indoor air concentration of PCB_{total} (Competenza GmbH rapport, 2013). Those results are in line with our findings. It was further concluded from the producer-conducted tests, that no significant reduction of PCB concentration in the wall paint had occurred 9 years after the encapsulation. Our results are inconsistent in this matter. We have observed up to 5% decrease of PCB concentration in the paint (and approx. 10% decrease in plaster under the paint) on one side of the sample, but not on the other side of the sample. The two paints (paint 1 and 2) had different initial PCB content (163 and 196 ppm respectively). It is unknown whether the different PCB content of those paints were due to exposure to different concentrations over the years, or whether the different paints had different affinity to PCB. Furthermore we have only measured marginal increase of PCB content in PERMASORB™ after 40 weeks, possibly due to insufficient extraction from this charcoal-containing wallpaper.

5 CONCLUSIONS

Both tested wallpapers, cTrap and PERMASORB™ Adsorber Wallpaper, applied on tertiary contaminated sources showed a potential to decrease indoor air concentration of PCB in contaminated buildings, with approx. 90% reduction after 40 weeks. The potential for extraction of PCBs from the contaminated materials stays unclear for both wallpapers.

ACKNOWLEDGEMENT

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